

PATENT SPECIFICATION

NO DRAWINGS

1.165.488



Date of Application (No. 23958/68) and filing Complete Specification: 20 May, 1968.

Application made in Canada (No. 992,026) on 2 June, 1967.

Complete Specification Published: 1 Oct., 1969.

Index at acceptance:—C3 G(1B2, 2B, 2C, C); C3 P(2C3, 2C8C, 2C18, 2D1A, 2D8, 2K7, 2K8, 2S2, 7C3, 7C8C, 7C18, 7D2A1, 7D8, 7K2, 7K8, 7S2, 8C3, 8C8C, 8C18, 8D3A, 8D8, 8K2, 8K7, 8S2)

International Classification:—C 08 f 41/12

COMPLETE SPECIFICATION

Modified Resins

We, POLYMER CORPORATION LIMITED, a company organized under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing homogeneous polymeric resin-carbon black compositions, with particular reference to ABS resin-carbon black compositions.

Acrylonitrile-butadiene-styrene resins, commonly known as ABS resins, are prepared either by a blending technique, by a graft copolymerization technique or by a combination of blending and graft copolymerization. In the blending technique a minor proportion of a nitrile rubber is blended with a major proportion of a styrene-acrylonitrile resin. In the graft copolymerization technique, a major proportion of a styrene-acrylonitrile monomer mixture is polymerized in the presence of a minor proportion of a diene rubber such as polybutadiene or styrene-butadiene copolymer, under conditions which effect graft copolymerization of the monomers onto the rubber. In the combination, a graft copolymer of styrene and acrylonitrile onto a butadiene rubber is prepared and then blended with styrene-acrylonitrile resin to give the desired composition in the final product. In the blending technique, of course, one ingredient is rubbery and the other ingredient is resinous. In the combination technique, the graft copolymer ingredient can be resinous or rubbery as desired. Because of their characteristically good impact strengths, combined with the good balance of their other properties, these resins are used in many applications including, for example, telephone housings, ladies shoe heels, extruded pipe, and automobile grilles and instrument bezels.

It is known that the addition of carbon [Price 4s. 6d.]

blacks to thermoplastic polymers in general, in a proportion of about 0.5 to 5%, preferably 2 to 3% by weight based on the weight of the polymer improves their resistance to the deleterious effects of ultra violet radiations; but in order to obtain good ultra violet resistance, the carbon black has to be homogeneously dispersed in the polymer. A good dispersion is difficult to achieve in some thermoplastic resins, especially with the finer particle size blacks which are preferred for this purpose. To obtain better distribution, it is known to use the black pigment in the form of a concentrate in a portion of the resin to which it is to be added and then to let it down, i.e. dilute it, to the required carbon black level by the subsequent blending in of further resin.

It is difficult to disperse carbon blacks in ABS resins and the difficulty of obtaining a homogeneous dispersion increases as the melt flow index of the resin is reduced (i.e. as the resin become stiffer and more viscous) and as the particle size of the black becomes finer. Moreover, when carbon black is poorly dispersed in an ABS resin, even in proportions as low as 1 or 2% by weight, the impact strength of the resulting compound is so drastically reduced that the resins become unsuitable for use in applications where impact strength is important. Additionally, the use of a carbon black concentrate in the ABS resin containing, for example, 15 to 35%, by weight of black, and diluting it with more of the resin to the 0.5 to 5% level does not produce a final compound having an acceptable impact strength.

It has been proposed to use as a concentrate a masterbatch of a rubbery butadiene-1,3-acrylonitrile copolymer and carbon black and to add it in sufficient amount to the ABS resins to obtain a final compound containing 2 to 3% of black. However, it has the disadvantage in the case of graft ABS

resins of introducing more rubber into the ABS resin composition thus destroying the carefully designed balance of resin to rubber characteristic of these resins and deteriorating some of the properties dependent on the resin/rubber ratio.

The object of the present invention is to overcome or reduce these disadvantages.

According to the present invention, there is provided a process of preparing homogeneous ABS resin-carbon black compositions which comprises the steps of preparing a homogeneous concentrate of 70—30 parts by weight of an ABS resin, 15—35 parts by weight of carbon black and 15—35 parts by weight of a material selected from alkyl aryl phosphites, waxes having melting points above 50°C, and mixtures thereof, and diluting the concentrate so formed with more ABS resin to give a homogeneous composition containing 0.5—5% (preferably 2—3%) by weight of carbon black. More of the same ABS resin can be used for diluting the concentrate or a different ABS resin can be used if desired.

It has been found that carbon black-containing ABS resins maintaining good impact resistance may be prepared in this manner. In actual practice a preferred method is to use both the alkyl aryl phosphite and the wax in the concentrate. Although the different components of the concentrate may be mixed in any order or simultaneously, it is essential that the amounts employed be within the specified limits and that the concentrate be mixed until its composition is substantially homogeneous before diluting. It is also essential that after diluting the mixing once again be continued until the composition attains a substantially homogeneous condition. Attainment of substantial homogeneity in the first of the mixing steps is most conveniently assured by the use of an internal mixer such as a Banbury mixer, while in the second it may be obtained with a Banbury mixer, a compounding extruder or on a mill.

The proportions of ABS resin in the concentrate is maintained between 30 and 70% by weight in order to obtain a concentrate which is easily processable on any conventional plastic compounding equipment. The proportion of the black in the concentrate must be between 15 and 35% by weight in order to obtain a homogeneous concentrate which is not too stiff and the proportion of the third ingredient must also be between 15 and 35% by weight in order to facilitate the dispersion of the black but it should not be present in too high an amount to avoid changing disadvantageously the balance of properties of the final black ABS product.

The process of the invention may be applied to any type of ABS resin. Its application to the graft type is particularly advantageous since the resin/rubber ratio is fixed

by the polymerization step and it is this ratio which determines many of the properties of the final product resin. The final product ABS resin generally contains about 5—40 weight % of a polymerized diene monomer, 15—40 weight per cent of a polymerized acrylic monomer and 25—80 weight per cent of polymerized vinyl aromatic monomer. The diene monomers include butadiene-1,3 and substituted butadiene-1,3 such as 2 - methylbutadiene - 1,3 and 2 - chloro - butadiene-1,3; the acrylic monomers include acrylic acid and its nitriles and esters such as acrylonitrile, methyl acrylate and methyl methacrylate; and the vinyl aromatic monomers include styrene, alpha-methylstyrene and chlorostyrene. Butadiene-1,3, acrylonitrile and styrene form a preferred combination of monomers. Thus, homopolybutadiene-1,3 or a copolymer of a major proportion of butadiene-1,3 with a minor proportion of styrene or acrylonitrile can form the rubbery portion of the ABS resin and a copolymer of a major proportion of styrene and a minor proportion of acrylonitrile may form the resin portion. The resin portion can either be polymerized in the presence of a smaller amount of the rubber to form the graft-type resin or it can be prepared separately and then blended with the rubber to form a blend-type resin. Suspension, solution, mass or aqueous emulsion polymerization processes may be employed in preparing the resins.

While any of the usual carbon blacks may be incorporated into the ABS resins by means of this invention, it is the small particle size blacks which provide the required ultra violet protection. The preferred blacks are channel blacks having an average particle diameter of less than about 25 millimicrons and preferably from about 10 to 25 millimicrons. As specific examples of commercially available carbon blacks of this type there may be mentioned those identified by the Trade-marks "Superba Special" and "Columbian 999".

The third component which is employed in the preparation of the concentrate is selected from alkyl aryl phosphites, waxes and mixtures of the two. The alkyl aryl phosphite is exemplified by compounds such as tricresylphosphite, tri(octylphenyl) phosphite, tri(nonylphenyl) phosphite, tri(decylphenyl) phosphite, di(octylphenyl) phosphite, octyl di(octylphenyl phosphite and tri(4 - methyl-2,6 - di[alphamethyl benzyl] phenyl) phosphite.

The wax component may be one obtained from animal, vegetable, mineral or synthetic origin. It generally consists of the solid esters of higher monohydric alcohols with higher monobasic carboxylic acids and generally includes free higher fatty acids and alcohols, and higher saturated hydrocarbons. Examples of suitable materials are known

commercially under the trade names or Trade-
marks: Japan wax, Beeswax, Candellila wax,
Carnauba wax, Ceresin wax, Acrawax C, and
Advawax 280. The wax should have a melt-
ing point above 50°C and preferably above
60°C.

This third component of the concentrate is
preferably used in the same proportions as
the carbon black. A particularly preferred con-
centrate contains about 50% by weight of the
resin, 25% by weight of carbon black and
25% by weight of the third component as
defined hereabove.

Best retention of impact strength in the
final products is attained by use of the alkyl
aryl phosphite without wax. However, since
a certain amount of fuming is encountered
resulting from the heat generated during the
blending step required to assure homogeneity
in the concentrate, it is preferred that this
step be carried out in an internal mixer or
on a mill provided with good exhaust means.
With waxes such fuming is not encountered
but the impact resistance of the final product
while still good, may be somewhat lower.
Mixtures of the two materials provide a bal-
ance of the advantages of each.

The invention is particularly useful for pre-
paring carbon black-containing grades from
ABS resins of low melt flow index, i.e., high
melt viscosity. Extruded pipes are made from
these materials. By low melt flow index it is
meant a melt flow index of less than 1 gram
per 10 minutes. Melt flow index is deter-
mined by measuring the weight of resin
which is extruded through an orifice having
a diameter of 0.0825 inches (2.095 milli-
meters) under a pressure of 10 kilograms
at a temperature of 220°C for 10 minutes.

The invention will be further described with
reference to specific examples.

EXAMPLE 1

A graft ABS resin containing about 20%
by weight of polymerized butadiene, 54%
of polymerized styrene and 26% of polymer-
ized acrylonitrile, the properties of which are
indicated under the heading "Natural" in
Table I, was used for the preparation of black
grades of the same black content but by
different processes. This resin, which was used
in powder form, contained 0.5% by weight
of tri(nonylphenyl) phosphite, known com-
mercially under the Trademark "Polygard",
as antioxidant.

(a) A first concentrate referred to as MB1,
was made with 75% by weight of the
resin powder and 25% by weight of
a fine particle size channel carbon black
having an average particle diameter of
160 Angstroms and a surface area of
370m²/g. This concentrate is outside the
scope of the present invention.

A number of other concentrates were made
containing 50% by weight of the same resin,
25% by weight of the same black plus the
following ingredients:

(b) 25% by weight of tri(nonylphenyl) phos-
phite antioxidant. This concentrate is re-
ferred to as MB2 and is within the scope
of the invention;

(c) 25% by weight of a synthetic wax, hav-
ing a melting point of 140—143°C.
available under the Trademark "Acra-
wax C". This concentrate is referred to
as MB3 and falls within the scope of
the invention.

(d) 25% by weight of an alkylated phenol
antioxidant available under the Trade-
mark "Naugawhite Powder". This con-
centrate is referred to as MB4 and is
outside the scope of the present inven-
tion;

(e) 25% by weight of dioctyl phthalate, a
well-known plasticizer. This concentrate
is referred to as MB5 and is outside the
scope of the invention.

1300 g. of each of these concentrates were
prepared in the same manner by charging
all the materials together into a Banbury
mixer and mixing them for 8 minutes at a
temperature of 300—350°F.

Each was then diluted to 2% by weight
of carbon black by milling at 325°F for 5
minutes with more of the same graft ABS
resin, and the properties of each of the
carbon black-containing final products are re-
ported in Table I under the heading of the
concentrate number used for preparing them.

Data relating to a carbon black-free blend
of 98% of the same resin with a further 2%
by weight of the tri(nonylphenyl) phosphite
milled together at 325°F for 5 minutes have
been included in the Table for the purpose
of comparison only. This blend is identified
as "Control".

TABLE I

	Natural	MB1	MB2	MB3	MB4	MB5	Control
Wax content of the final grade (% by weight)	0	0	0	2	0	0	0
Polygard content of the final grade (% by weight)	0.5	0.5	2.5	0.5	0.5	0.5	2.5
Black content of the final grade (% by weight)	0	2	2	2	2	2	0
Tensile strength at break (in psi)	—	3,890	3,570	3,290	3,820	3,140	3,810
MFI (g./10 min.)	0.47	—	—	—	—	—	—
Rockwell hardness (R scale)	88	97	97	95	98	95	92
Vicat Softening Point (°C.)	105	107	103	105	106	102	103
Charpy impact strength (ft./lbs./in. notch)							
73°F	11.5+	8.70	11.5+	11.5+	5.36	7.38	11.5+
-20°F	8.75	2.68	8.18	6.28	1.94	2.48	9.32
-40°F	7.16	2.30	4.10	3.08	1.10	1.99	7.84

NB: 11.5+ means that the actual impact strength of the resin tested was over the maximum of 11.5 measurable with the Charpy apparatus used.

From this Table, the following conclusions may be drawn:

- 5 (a) A graft ABS resin of high impact strength (Natural) retains its impact strength after the introduction of a further 2% of an alkaryl phosphite (Control).
- 10 (b) But this same resin (Natural) suffers a sharp reduction in impact strength when carbon black alone is introduced (MB1). However, when the carbon black is introduced along with a further 2% of the Polygard (MB2) or the wax (MB3), loss in impact strength is avoided.
- 15 (c) The type of agent required for successful incorporation of the carbon black appears to be highly specific since other materials having similar functions, such as another antioxidant (MB4) or a plasticizer (MB5) do not prevent but actually
- 20 increase the loss of impact strength.

EXAMPLE 2

- 25 This example illustrates the use of different waxes at the minimum amount level required to obtain the improvement of the present invention.

A graft ABS resin containing 21.5% by weight of polymerized butadiene, 51% of polymerized styrene and 27.5% of polymer-

ized acrylonitrile, the properties of which are indicated under the heading "Natural" in Table II, was used for the preparation of different concentrates and for diluting these concentrates to 2% by weight of black under the same conditions as described in Example 1. This resin which was used in powder form, contained 0.5% by weight of tri(nonylphenyl) phosphite as antioxidant.

Concentrates MB1, MB2 and MB3 which fall within the scope of the present invention were made with 60% by weight of the above-defined resin, 25% by weight of the same carbon black as in Example 1 and 15% by weight respectively of Carnauba Wax, Beeswax or Japan Wax.

Concentrate MB4 was made with 75% by weight of resin and 25% of the same black and is outside the scope of the invention since no further additive was used.

Concentrates MB5 and MB6, which fall outside the scope of the invention were made with 60% by weight of the resin, 25% by weight of the black and 15% by weight respectively of Drapex 68 and Paraplex (Registered Trade Mark) G54. These concentrates fall outside the scope of the invention since the latter two materials are neither phosphites nor waxes as defined.

Carnauba Wax, a vegetable wax comprising

the myricyl ester of cerotic acid is a yellowish hard brittle solid of melting point 84—86°C.; Beeswax, an animal wax comprising the palmitic ester of myricyl alcohol, is an amorphous, yellow to white solid of melting point 63—64°C.; and Japan Wax is a pale yellow solid vegetable wax of melting point about 53°C.

Drapex 68 is an epoxidized soybean oil and a pale yellow liquid solidifying at 0°C, and Paraplex G54 is an intermediate mole-

cular weight polyester which is a clear viscous liquid solidifying at 4°C.

Concentrate MB7 was made with 62.5% by weight of the resin, 25% by weight of the black and 12.5% by weight of Japan Wax. This concentrate is outside the scope of the invention because the amount of wax is too low.

The properties of the different final product black grades all containing 2% by weight of black are given in Table II.

TABLE II

	Natural	MB1	MB2	MB3	MB4	MB5	MB6	MB7
Wax content of the final grade (% by weight)	0	1.2	1.2	1.2	0	0	0	1
Polygard content of the final grade (% by weight)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Black content of the final grade (% by weight)	0	2	2	2	2	2	2	2
Tensile strength at break (in psi)	4,530	4,590	3,870	3,590	4,210	3,870	3,820	3,880
Melt flow index (in g/10 min.)	0.8	0.24	0.25	0.30	0.30	0.12	0.30	0.29
Rockwell Hardness (R scale)	98	98	98	100	102	96	97	99
Vicat softening point (—C°)	—	—	—	106	105	—	—	107
Charpy impact strength (in ft./lbs./in. notch) 73°C —20°F	11.5+ 7.2	10.39 3.64	9.81 3.66	11.1 3.80	5.60 1.71	2.87 0.96	5.11 1.19	7.78 2.11

See Note to Table I.

From this Table, the following conclusions may be drawn:

- (a) The high impact strength, low melt flow index (Natural) grade of ABS resin suffers a drastic loss in impact strength when carbon black is introduced in the absence of the additive (MB4).
- (b) When the addition of the carbon black is accompanied by the addition of a wax according to the invention (MB1, MB2 and MB3), the impact strength of the final black grade is clearly improved over the impact properties of the same black grade made from a concentrate which did not contain any wax (MB4).
- (c) However, when too low an amount of wax is used in the concentrate (MB7), the degree of improvement is not considered to be acceptable.
- (d) The choice of the agents to be used in the invention (MB1, MB2, or MB3) is highly selective since other materials used as plasticizers (MB5 and MB6) in the same amounts do not permit obtaining the same results, as far as impact strength is concerned.

EXAMPLE 3

This example illustrates the use of a mixture of wax and alkyl aryl phosphite in the required proportions to obtain the improvement of the invention.

A graft ABS resin containing 13.5% by weight of butadiene, 61.5% by weight of

styrene and 25% by weight of acrylonitrile was used for the preparation of different concentrates. This resin, used in powder form, contained 1.50% by weight of tri(nonylphenyl) phosphite ("Polygard") as antioxidant.

Concentrate MB1 which falls within the scope of the invention was made by blending 60% by weight of the resin, 20% by weight of the carbon black of Example 1, 10% by weight of Acrawax C and 10% by weight of tri(nonylphenyl) phosphite.

Concentrate MB2 which falls also within the scope of the invention was made with 50% by weight of the resin, 25% by weight of the carbon black, 12.5% by weight of Acrawax C and 12.5% by weight of tri(nonylphenyl) phosphite.

In concentrate MB3, carbon black was the only material added to the resin.

These concentrates were prepared in the same manner by charging the carbon black, tri(nonylphenyl) phosphite and wax to a Banbury mixer at 300—350°F mixing for 2 minutes, then adding the resin powder and continuing mixing for another 8 minutes. While still hot, the concentrate was sheeted out on a hot mill.

Each of these concentrates was then diluted to 2% by weight of carbon black by milling for 5 minutes at 325°F with more of the graft ABS resin and the properties of each of these black grades are reported in the following Table under the heading of the concentrate numbers used for preparing them.

TABLE III

	Natural	MB1	MB2	MB3
Wax content of the final grade (% by weight)	0	1	1	0
Polygard content of the final grade (% by weight)	1.5	2.5	2.5	1.5
Black content of the final grade (% by weight)	0	2	2	2
Tensile strength at yield (in psi)	5,000	4,230	4,490	4,840
Melt flow index (in g/10 min.)	11.5	18.0	10.1	6.7
Rockwell hardness (R scale)	—	106	100	105
Vicat softening point (°C.)	—	104	100	104
Charpy impact strength (ft./lbs./in. notch)				
73°F	4.1	6.3	6.16	2.96
—20°F	0.92	—	1.43	0.92
—40°F	—	—	0.84	—

From this Table, it is seen that the medium impact, medium flow grade of graft ABS resin (Natural) has its impact properties badly impaired by the introduction of black by conventional means (MB3). The use of concentrates containing a mixture of wax and tri-(nonylphenyl) phosphite according to the invention surprisingly improves the impact properties of the final black grade not only over that obtained by conventional means but also over the unadulterated original resin (Natural).

WHAT WE CLAIM IS:—

1. A process of preparing homogeneous ABS resin-carbon black compositions which comprises the steps of preparing a homogeneous concentrate of 70—30 parts by weight of a first ABS resin, 15—35 parts by weight of carbon black and 15—35 parts by weight of a material selected from alkyl aryl phosphites, waxes having melting points above 50°C, and mixtures thereof, and diluting the concentrate so formed with a second ABS resin, the same as or different from said first ABS resin to give a homogeneous composition containing 0.5—5% by weight of carbon black.
2. A process as claimed in claim 1 wherein at least one of said first and second ABS resins comprises 5—40 weight % of a polymerized diene monomer, 15—40 weight % of a polymerized acrylic monomer and 25—80% by weight of a polymerized vinyl aromatic monomer.
3. A process as claimed in claim 1 or claim 2 wherein at least one of said first and second ABS resins comprises a graft copolymer of a vinyl aromatic compound and an acrylic nitrile compound grafted onto a pre-formed diolefinic polymer.
4. A process as claimed in any of the preceding claims wherein said second ABS resin is the same as said first ABS resin.

5. A process as claimed in any of the preceding claims wherein the alkyl aryl phosphite is tri(nonylphenyl) phosphite.

6. A process as claimed in any of the preceding claims wherein the carbon black has an average particle diameter of from 10—25 millimicrons.

7. A process as claimed in Claim 1 substantially as hereinbefore described.

8. A polymeric resin-carbon black composition prepared by the process of any of the preceding claims.

9. A composition comprising a homogeneous mixture of 90—99 parts by weight of a resinous polymer comprising 5—40 weight % of a polymerized diene monomer, 15—40 weight % of a polymerized acrylic monomer and 25—80 weight % of a polymerized vinyl aromatic monomer, with 0.5—5 parts by weight of a carbon black and 0.5—5 parts by weight of a material selected from alkyl aryl phosphites, waxes having a melting point above 50°C, and mixtures thereof, whenever prepared by a process as claimed in any of Claims 1 to 7.

10. A composition as claimed in Claim 9 wherein the resin comprises a graft copolymer of 25—80% by weight of styrene and 15—40% by weight of acrylonitrile graft copolymerized onto 5—40 weight % of a butadiene-1,3 polymer.

11. A composition as claimed in Claim 9 or Claim 10 wherein the carbon black has an average particle diameter of from 10—25 millimicrons.

12. A composition as claimed in Claim 9 substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.